



no 452754

## PATENT SPECIFICATION no 18,818/70

Class (2) 09.13; 07.03  
Int. Cl. (2) C07D; B01J

Application Number (2) 18818/70  
Lodged (2) 14th August 1970

Complete Specification  
entitled (2) PROCESS FOR THE PRODUCTION OF ETHYLENE  
OXIDE

Lodged (2) 14th August 1970  
Accepted (2) 28th August 1974  
Published (2) 17th February 1972

Convention Priority (2) Italy, 28th August 1969, 21262A/69; 20th July 1970,  
26014A/70; 28015A/70 and 28015A/70

Applicant (2) SNAM PROGETTI S.p.A.

Actual Inventor (2) CARLO PICCINI;  
MORELLO MORELLI and  
PIERLUIGI REBORE

Related Art (2) 24692/53 09.3; 07.9  
166901 (27163/54) 09.8; 09.13  
278697 (36255/53) 09.10

The following statement is a full description of the invention, including the best method of performing it known  
to us :

X637-78-1D-21PC

S. G. Adams, Government Printer, Chicago

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The present invention relates to a process for the production of ethylene oxide by catalytic oxidation of ethylene.

The preparation of ethylene oxide by oxidation of ethylene in the presence of suitable catalysts is well known.

These known processes can be divided into two groups, in the first one the oxidation is carried out in the presence of air, in the second one in the presence of pure oxygen.

In both cases use is made of catalysts known in the art as "silver catalysts": metallic silver is in fact the element that promotes the oxidation of ethylene to ethylene oxide.

It is also known that in the preparation of these silver catalysts, may be deposited on suitable supports and in order to improve their activity.

A known industrial process for producing ethylene oxide comprises reacting a mixture containing ethylene in the range from 1 to 30%, preferably from 2 to 10%, and oxygen (or air) in the range from 2 to 8%, on a silver catalyst bed at a temperature from 150 to 400°C and at a pressure in the range from 0.7 to 35 atmospheres. To overcome low yields an inhibitor is used, for example an halogenated organic compound for instance dichloroethane. Contact times ranges generally from 0.1 to 15 seconds.

We have now surprisingly found out that it is possible to accomplish a very profitable industrial process if a very concentrated ethylene feed is allowed

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to contact a silver catalyst, as hereinafter described.

According to the present invention there is provided a process for the oxidation of ethylene to ethylene oxide with pure oxygen or a mixture containing oxygen at a temperature ranging from 100 to 400°C and at a pressure ranging from 0.7 to 35 atmospheres comprising reacting ethylene at a concentration of from 40 to 80% in the presence of a catalyst constituted by Ag, Cu and Ba, the ratio between the gram atoms of Ag and the sum of gram atoms of calcium and barium being equal to or greater than 1.

The most preferred ethylene/oxygen ratio in the feed is higher than 3.

With reference to the catalyst employed in the process of the present invention it is not possible to utilize all known catalysts; some of them have little activity and present low selectivity; a general but not limitative criterion for the choice of the catalyst may be based on the fact that the best catalyst seem to be the ones having as active part silver and other compounds and/or elements as pure metals, metalloids, halogens or their compounds known for affecting oxidation reaction.

The elements and/or compounds which promote the ethylene oxide formation reaction are alkaline earth metals such as calcium and barium. Such elements and/or compounds can be supported on a carrier and, if the support is alumina, it should have a good porosity to allow the active part (Ag, Cu and Ba) to be well distributed and fixed thereon.

Catalyst can be used as powder too, that is the active part only (e.g. for fluidised beds) without support.

Preparations of catalysts according to the present invention are illustrated in the examples.

The process of the present invention shows that an increase of ethylene concentration causes a corresponding

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increase of selectivity and, contrarily to what generally is cited in literature, a reaction velocity decrease.

When the oxidation operation is carried out with the ethylene concentration of the present invention it is usually noticeable that the material constituting the reaction equipment, saturated hydrocarbons possibly present in the feed or rare gases present have little or no detrimental effect on the present process. Thus control of the reactants is usually only necessary to provide good results. In fact it has been found carbon dioxide need not be precluded from the process of the present invention. This is surprising as at low ethylene concentrations (ie. below 1%) carbon dioxide has an undesirable effect on the catalyst activity.

Acceptable levels of inerts for example as saturated hydrocarbons and rare gases such as carbon dioxide is 7% to 60% of the gaseous mixture, preferably between 1% and 50% and most preferably at least 20%.

It has been also surprisingly found that ethane has little or no detrimental effect on the present process. Conflicting statements have been made in the prior art as to the presence of ethane in the production of ethylene oxide. In U.S. Patent 3,119,657 it is stated that hydrocarbons should be withdrawn from the feed mixtures while French Patent 2,555,797 states ethane from 4 to 40% by volume of the feed mixture can be present without undesirable effects. Thus it is not clearly apparent why in the present process ethane can be present without incurring disadvantages. Perhaps the only factors which may affect the situation are the ethylene concentration and

the catalyst used.

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With regard to the catalyst used in the present invention the catalyst comprises silver, calcium and barium such that the gram atom ratio of silver to calcium plus barium is at least one. Preferably the gram atom ratio of silver to calcium plus barium is 4 to 15. Most preferably the gram atomic ratio of Ag/Ca/Ba is 15/2.5/1.

In the preferred embodiment of the present invention the active part that is silver, calcium and barium is supported on a carrier. For this purpose ceramic carriers such as alumina can be employed. When alumina is used it must have a suitable porosity and preferably be macroporous.

Another important factor is the preparation technique of these compositions.

The best technique consists substantially in preparing a solution of water soluble salts in water, said salts being constituted by metals of the active part of the catalysts, precipitating said metals in the solution so as to obtain a powder of active part, preparing a suspension of this powder, treating the carrier with said suspension and finally drying and heat treating the catalyst obtained.

The use of high ethylene concentration in the feed simplifies the operating cycle and allows, as before mentioned, to accomplish ethylene oxide production in very advantageous conditions.

A simplified flow-scheme of the process according to our invention is represented in fig. 1 where to a reactor 1 containing silver catalysts, ethylene and oxygen or mixture containing oxygen are sent through line 2; ethylene and oxygen or mixture containing oxygen are

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introduced through inlets 3 and 4 respectively; from the reactor 1, a mixture containing ethylene oxide and unreacted compounds are withdrawn. Said stream is sent to the tower 5 where the ethylene oxide is absorbed while unreacted compounds are withdrawn from the top of tower 5 and partially recycled, because of their high ethylene content, directly to the reactor 1 through line 6. The other part said unreacted compounds are sent to tower 8 where the ethylene is scrubbed and where a  $\text{CO}_2$  and inert gases purge is provided; the ethylene recovered in 10 is recycled to reactor 1 through line 9.

Through inlet 7 water for removing ethylene oxide is introduced.

Between tower 5 and 8 an intermediate stage, e.g. to scrub  $\text{CO}_2$ , and also several oxidation reactors and other conventional equipment known in the art may be provided.

The process according to our invention allows to obtain high selectivity values increasing with the ethylene concentration; furthermore because of the higher limits of the concentration range (namely 40-80%) this process allows to operate, if it is convenient, -unlike conventional known processes - without inhibitors. Thus an important advantage is achieved because the ethylene oxide leaving the reactor does not contain undesirable impurities.

When the operation is carried out in presence of an inhibitor, this can be chosen in the wide class of the compounds known in the art for this purpose as, for instance, the halogenated organic compounds and among

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then dichloroethane is suggested. Practically no limits for the amount of employed inhibitors are considered in the process according to the present invention.

By way of example the amounts of inhibitor are usually lower than 0.3 ppm by volume in the whole gaseous mixture and preferably between 0.01 and 0.3 ppm. However higher concentrations, up to 10-30 ppm, may be employed.

Other advantages arise due to the fact it is possible to eliminate the  $\text{CO}_2$  scrubber required by prior art processes. Also as stated previously it is not usually necessary to remove ethane from the feed mixture. This allows for improvement in operating costs as special feeds and consequential equipment are not required.

If it is noticed that ethane does begin to accumulate in the process it can always be removed by the purge.

A further advantage is that it is possible to operate with oxygen contents even higher than 5% and up to the explosivity limits of the mixtures and it improves the plants productivity.

Another remarkable advantage is that with the same productivity the process according to our invention can operate at a temperature lower than in conventional processes; the temperature may reach even  $30^\circ\text{C}$  and sometimes lower values, extending in this way the catalyst life. Therefore in the process according to our invention the reaction temperature ranges from 100 to  $400^\circ\text{C}$ .

The present invention will now be further illustrated by the following examples.

The tests of the examples have been carried out

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by gas-chromatography.

EXAMPLE 2

Some tests have been carried out at constant temperature and at several ethylene contents in the feed with a 5/16" catalyst prepared in the following way:

100 grams of silver nitrate, 24 grams of tetrahydrate calcium nitrate and 21 grams of barium nitrate were dissolved in 1500 cc of deionized water (Ag/Ca/Ba ratio is 15/2.5/1).

The obtained solution, which may be opalescent because of the presence of small traces of silver chloride that may form, was filtered with adsorbents.

42 grams of anhydrous sodium carbonate



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were dissolved in 500 cc of distilled and purified water with 2 grams of silver nitrate.

The obtained solution was filtered.

Before mixing the two said solutions, a small amount of calcium chloride (about 10 mg) was added to the nitrate solution.

The coprecipitation of silver calcium and barium carbonates was carried out adding, under rapid mixing, the sodium carbonate solution to the nitrate solution.

Precipitation of the carbonates in a very subdivided form was obtained. Said solution was filtered and the precipitate washed with deionized water and dried in a stove, in presence of a small air flow, for some hours at a temperature of 110°C.

About 120 grams of catalytic powder were obtained, said powder was finely milled in a hammer mill then the milled catalytic powder was sprinkled on the carrier.

The carrier was a commercial one, e.g. alumina having the following characteristics:

(Alumina S.A. 5218 by Norton):

Shape: 1/16" diameter Spheres

Composition:

Al <sub>2</sub> O <sub>3</sub>	85.90	SiO <sub>2</sub>	0.10	Na <sub>2</sub> O	0.03
SiO <sub>2</sub>	12.40	MgO	0.60	K <sub>2</sub> O	0.50
Fe <sub>2</sub> O <sub>3</sub>	0.80	CaO	0.40		

Physical/chemistry characteristic (X Ray):  $\gamma$  - Al<sub>2</sub>O<sub>3</sub>

+ Mullite

Porous structure; porosity by volume = 50.8%

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pore radii = 100 - 700 microns

This carrier presented a porous structure particularly suitable for the purpose as it allowed to obtain a complete penetration of the catalyst even into the inner parts of the spheres.

Of course other types of allumina or of carrier presenting the same properties could be used.

The inhibition was carried out mixing the obtained catalytic powder with 800 grams of a 30% ethylene glycol solution and treating the obtained suspension with 550 grams of carrier kept under stirring to facilitate a uniform inhibition.

The obtained matter was dried and activated under controlled air flow, at about 350°C, for some hours.

Said catalyst, for the execution of the cited tests, has been put in a reactor having a 1 m <sup>length</sup> and a 1" diameter, kept at constant temperature by double jacket stirred by nitrogen flow.

The operating conditions were the following:

Pressure : atmospheric  
 Temperature : 171°C  
 Catalyst amount : 484 grams, 9.5% of Silver  
 Flow rate : 210 ml/hr  
 Contact time : 4.6. sec

The results of the tests were:

No. of the tests	%O in the feed	%C <sub>2</sub> H <sub>4</sub> in the feed	reaction velocity C <sub>2</sub> H <sub>4</sub> moles reacted/hr	Selectivity % moles	T°C
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1	5	40	129	63	171
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2	5	60	60	74	172
3	5	77	55	76.5	172

**EXAMPLE 2**

In the same reactor, at the same operating conditions (except for the temperature) and <sup>the same</sup> ~~same~~ of the same catalyst described in example 1, tests have been carried out at constant reaction velocity, varying the ethylene concentrations and at increasing temperature.

The results obtained were the following one :

No. of the tests	t°C	%O <sub>2</sub> feed	%C <sub>2</sub> H <sub>4</sub> feed	reaction velocity moles of C <sub>2</sub> H <sub>4</sub> reacted/h <sup>2</sup>	Selectivity % moles
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1	155	5	5	55-60	57
2	160	5	40	55-60	72.5
3	166	5	60	55-60	76.5
4	172	5	77	55-60	76.5

**EXAMPLE 3**

A series of tests has been carried out in a stainless steel reactor having an inner diameter of 16 mm and a length of 28 cm provided with an outer jacket wherein a silicon oil, as thermostatic fluid, circulated. The employed catalyst was constituted by a Ag, Cu, Ba carbonates powder prepared as described in example 1 and calcined at 300°C in air flow. The operating temperature and pressure have been kept respectively at 150°C and 1 atmosphere.

The tests have been carried out by loading the reactor with 24.5 grams of catalyst (height of catalyst bed = 14.5 cm.) and feeding to the reactor

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5 lit/hr. of gaseous mixtures containing 5% of  $O_2$   
and from 7% to 60% of ethylene.

The contact time was of 12.6 seconds.

The results of the test were the

following :

No. of the test	% $O_2$ feed	% $C_2H_4$ feed	reaction velocity of $C_2H_4$ reacted/hr.	Selectivity % moles
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1	5	32	1.50	73.6
2	5	43	1.30	74.9
3	5	60	0.78	77.4

For 7% ethylene concentration the selectivity was about 65% and for 22% of ethylene it did not exceed 70%.

#### EXAMPLE 4

In the same reactor and with the same catalyst of example 3, a series of test with different concentrations of ethylene and keeping constant the reaction velocity, by means of the temperature, has been carried out.

The feed mixtures had a constant content of oxygen of about 5% while the ethylene concentration ranged between 7% and 60%; the contact time was of 12.6 seconds, as in example 3.

The obtained results were the following

ones:

No. of the test	°C	% $O_2$	% $C_2H_4$	reaction velocity moles $C_2H_4$ reacted/hr.	Selectivity % moles
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1	173.5	5	32	3.70	67.6
2	178	5	43	3.67	69.2
3	183	5	60	3.75	71.0
4	184	5	73	3.75	73.2
5	185	5	83	3.76	75.4
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The selectivity increased from about the 57% for feed ethylene concentration of 7%, not exceeding any how 62% when the ethylene concentration was about 80%.

**EXAMPLE 2**

To control the influence of the material with which the reactor was built, two series of tests have been carried out with the same catalyst and with ethylene concentration ranging between 40% and 60%. In these series of tests the same stainless steel reactor of example 1 and an iron reactor with the same geometric dimensions had been employed. The employed catalyst is similar to the one described in the example 1. The obtained results of the tests carried out in the stainless steel reactor were:

No. of test	T <sup>o</sup>	%O <sub>2</sub> feed	%C <sub>2</sub> H <sub>4</sub> feed	reaction velocity moles C <sub>2</sub> H <sub>4</sub> reacted/hr	Selectivity % moles
1	174	5	40	101,3	70,8
2	174	5	60	71,8	74,8
3	174	5	77	53,1	76,6

the results of the test carried out in the iron reactor were:

No. of test	T <sup>o</sup>	%O <sub>2</sub> feed	%C <sub>2</sub> H <sub>4</sub> feed	reaction velocity moles C <sub>2</sub> H <sub>4</sub> reacted/hr	Selectivity % moles
1'	174	5	40	90,0	70,3
2'	174	5	60	63,6	74,6
3'	174	5	77	53,5	77,5

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EXAMPLE 6

For checking the influence of ethane on the reaction, a test has been effected with 60% ethylene, 5% of  $O_2$ , 10% of ethane, 25% of  $H_2$ ; this test has been compared with a test effected with 60% of ethylene, 5% of  $O_2$  and 35% of  $H_2$ .

Both tests have been carried out in the same reactor and at the same operating conditions of example 1; also the catalyst is similar to the one described in example 1.

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The results of the test were the

following:

- tests without ethane:

temperature =  $175^{\circ}\text{C}$ reaction velocity = 80.3 moles reacted  $\text{C}_2\text{H}_4/\text{hr}$ .

selectivity = 75.8% moles.

- test with 10% of ethane:

temperature =  $175^{\circ}\text{C}$ reaction velocity = 89.1 moles reacted  $\text{C}_2\text{H}_4/\text{hr}$ .

Selectivity = 72.6% moles.

EXAMPLE 7

For checking the influence of argon on the reaction two tests have been carried out in the reactor, with the catalyst and at operating conditions described in the example 1; the concentrations of the two tests were:

1) 60%  $\text{C}_2\text{H}_4$  - 5%  $\text{O}_2$  - 35%  $\text{N}_2$ 2) 60%  $\text{C}_2\text{H}_4$  - 5%  $\text{O}_2$  - 35% Ar.Both tests have been carried out at  $172^{\circ}\text{C}$ .

The obtained results for the reaction velocity and selectivity were:

	reaction velocity $\text{C}_2\text{H}_4$ reacted/hr	selectivity % moles
Mixture 1)	79.1	74.1
Mixture 2)	79.6	75.8

In a test in which nitrogen or argon have been replaced by carbon dioxide at the same concentration, the obtained selectivity was substantially equal to the selectivity of the tests with nitrogen or carbon dioxide.

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EXAMPLE 8

Preparation of the catalyst

For this example use has been made of technique of example 1.

A precipitation or a co-precipitation in form of carbonates of the elements constituting the active part has been carried out starting from the corresponding solutions of nitrates or of other water soluble salts. Carbonates were so obtained in an extremely subdivided state and were filtered, washed with deionized water and dried in a stove in a weak air flow for some hours at a temperature of about  $110^{\circ}\text{C}$ .

Said materials were then deposited on the carrier. An carrier was made of the allumina of example 1; said allumina had the following characteristics:

Shape :  $5/16''$  diameter spheres.

Physical chemistry characteristic (X Ray)  $\gamma\text{-Al}_2\text{O}_3$  + Noilite

Porous structure; porosity by volume = 50.6%

Pores radii = 100 - 700 microns

The inhibition of the active part was realized preparing a suspension of said part in mixture water/ethylene glycol and treating the carrier with this suspension.

Then the obtained material was dried in a controlled air flow at a temperature of about  $350^{\circ}\text{C}$  for some hours. With this technique the catalysts numbered from 1 to 9 have been prepared.

With reference to table 1 the catalyst



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numbered 4 this is an example of separated precipitation on one hand Ag and on the other hand the two promoters (Ca and Ba) and mechanical mixing of the precipitate while for the catalysts 7, 8 and 9 little amounts of  $\text{CaCl}_2$ , generally about  $5 \cdot 10^{-4}$  gr. per Ag gr., have been added.

In all said catalysts the Ag content is 10% by weight of the finished catalyst.

Variants of this preparation are those in which the preparation of precipitates different from carbonates are provided; for instance the precipitation in form of oxides or the inhibition without using polyoxidic alcohols, as for instance a ethylene glycol, or also the replacement of the operation of co-precipitation with a precipitation of the single constituents followed by a mechanical mixing of all the precipitates.

Another series of catalysts has been prepared with the solution technique.

It consists in preparing an organic salt of the silver and of the possible promoters (preferably lactates are prepared) and in impregnating the carrier with said solutions; during the operation the temperature was kept at about  $90 - 95^\circ\text{C}$  with variable durations according to the type of carrier and anyway not longer than one hour; afterward the solution was withdrawn and the impregnated material was kept at  $90 - 95^\circ\text{C}$  for about 15 minutes.

The catalyst was then put in a stove for 12 hours at  $70 - 80^\circ\text{C}$  in a weak air flow; then it was

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calcined at 320°C for about 5 hours in a controlled air flow.

With this technique the catalysts numbered from 10 to 15 have been prepared.

All the catalysts from 1 to 15 have been employed for the production of ethylene oxide with feeds containing either 5% to 60% of ethylene and 5% of oxygen. The results of the tests are shown in table 1 where possible variants of the compositions of the feed mixture are indicated. The tests have been carried out in a conventional reactor having a 1 m length, a 1" diameter kept at constant temperature by a cooling jacket kept in agitation by a nitrogen flow and in a such way to have the same productivity i.e. the same number of moles of ethylene reacted per catalyst unit volume and per hour.

Practically the productivity was kept at a rate of 180 - 200 moles of ethylene per liter of catalyst per hour.

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Table 1

Catalyst No.	Atomic ratio Ag/Da/Da	$\tau$ (dependence) $\sigma$ <i>S (selectivity)</i>		$\sigma$ mol.	Carrier	Silver, % by weight
		5% $C_2H_4$	60% $C_2H_4$			
		without 0.06% inhibitor in hexane	without 0.12% inhibitor in hexane			
1	15/0/0	46 <sup>180</sup>	67 <sup>190</sup> 77 <sup>220</sup>		55/15" spheres of Al <sub>2</sub> O <sub>3</sub> + NaCl + pores 10-50.8% by volume pores radii 100 + 700 microns	20
2	15/0/1	47 <sup>166</sup>	67 <sup>173</sup> 75 <sup>185</sup>		"	"
3	15/2/50	46 <sup>166</sup>	70 <sup>170</sup> 76 <sup>180</sup>		"	"
4	15/25/1	(a) 40 <sup>161</sup>	74 <sup>163</sup> 78 <sup>172</sup>		"	"
this	15/25/1	32 <sup>168</sup> 70 <sup>172</sup>	65 <sup>169</sup> 75 <sup>177</sup>		"	"
5	15/0/35	45 <sup>182</sup> (b) 61 <sup>195</sup>	68 <sup>177</sup> 74 <sup>196</sup>		"	"
6	15/3.5/0	42 <sup>170</sup> 72 <sup>203</sup>	67 <sup>176</sup> 74 <sup>198</sup>		"	"
7 (a)	15/0/0	(a) 50 <sup>220</sup>	65 <sup>197</sup> 72 <sup>212</sup>		"	"
8 (a)	15/0/2	68 <sup>199</sup>	61 <sup>199</sup> 70 <sup>209</sup>		"	"
9 (a)	15/2.5/0	(a) 60 <sup>190</sup>	66 <sup>179</sup> 72 <sup>185</sup>		"	"
10	200/0/1	(a) 35 <sup>126</sup>	57 <sup>212</sup>		CHP, 2 3/16" by CARBO-BRAND CO.	14.6
11	14/0/2	34 <sup>195</sup>	47 <sup>201</sup> 65 <sup>219</sup>		Carbonum diam, 6 pores = 50 + 250	14.7

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12	24/0/0			(a) 62 <sup>196</sup>	Alumina LASH by Norton $\phi$ pores = 2 $\mu$ total porosity 0.46 cc/gr	14.9
13	15/2.5/2	35 <sup>192</sup>	(b) 60 <sup>215</sup>	57 <sup>204</sup> 66 <sup>203</sup>	Alumina, 3/16" $\phi$ pores 0.50-250 total porosity 0.25 cc/gr	8
14	24/0/2	35 <sup>199</sup>	60 <sup>244</sup>	54 <sup>209</sup> 61 <sup>212</sup>	Extruded cylinder Alumina $\phi$ 2 mm length 8mm pores 0.15-300 total porosity 0.18 cc/gr	15.1
15	14/0/2	34 <sup>195</sup>	52 <sup>230</sup>	52 <sup>205</sup> 61 <sup>205</sup>	Alumina 1/16" pores 0.50-250 total porosity 0.25 cc/gr	8

(\*\*) carriers with different porosity may be suitably employed.

in table 1 we mean:

S Selectivity moles %

T<sup>o</sup> Reaction temperature

(a) test effected with a mixture of: 5% C<sub>2</sub>H<sub>4</sub>, 6.5% CO<sub>2</sub>, 65% N<sub>2</sub>

(b) Test effected in presence of 0.03 ppm of inhibitor

(c) catalyst prepared with GaCl<sub>3</sub>

(d) test effected with a mixture containing 0.20 ppm of inhibitor.

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**EXAMPLE 2**

To a reactor made of carbon steel, kept at constant temperature with downflow and operating at a pressure of 18 kg/cm<sup>2</sup>, several mixtures have been fed whose compositions are indicated in table 2. The table shows the operating temperatures and the obtained results. The other operating conditions have been the same in all the tests so as to make possible a confrontation of them. Further the catalyst employed in the tests indicated in table 1 is the same of example 1.

**TABLE 2**

%C <sub>2</sub> H <sub>6</sub>	%O <sub>2</sub>	%C <sub>2</sub> H <sub>4</sub>	°C	reported C <sub>2</sub> H <sub>4</sub> moles/hr.	Selectivity moles %
4.9	4.0	—	216	7.2	71.7
5.0	4.2	10.4	205	6.6	62.8
20.3	4.0	—	209	7.2	75.3
20.2	4.1	10.0	207	7.2	71.7
39.4	4.1	—	213	6.6	76.1
40.1	4.1	10.5	215	7.0	74.7
139.4	3.9	—	233	10.5	71.3
40.4	4.0	10.7	233	10.0	72.8
40.1	4.0	—	243	11.3	69.5
39.7	4.0	30.7	233	11.3	67.6
40.2	10.3	30.8	233	13.4	69.4
40.7	4.0	—	253	12.2	66.5
40.8	4.1	10.6	243	12.2	67.3

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In each test, beside the indicated components, dichloroethane was fed, as inhibitor, at a concentration of 0.03 ppm by volume with respect to the mixture; the remainders were inerts, above all nitrogen. The obtained results clearly showed the following trends: at low ethylene concentration (about 5%) the presence of ethane deeply decreased the selectivity; said effect decreased with increasing ethylene concentrations till practically to zero for ethylene concentration of about 40%.

**EXAMPLE 10**

In a stainless steel reactor, kept at constant temperature with dowtherm and operating at a pressure of 18 kg/cm<sup>2</sup>, seven catalysts have been tested. The ones numbered from 1 to 6 in table 3 were similar to the ones described in example 1; the one numbered 7 was of the type described in U.S.P. 2,477,435.

The mixtures compositions are given in table 3.

Beside the cited components also dichloroethane as inhibitor at a concentration of 0.03 ppm by volume with respect to the mixture was fed, the remainders were inerts and especially nitrogen.

The other operating conditions were identical in all the tests so as to make them comparable.

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Table 3

Catalyst no.	%O <sub>2</sub>	%CO <sub>2</sub>	%O <sub>2</sub>	%O	reacted C <sub>2</sub> H <sub>4</sub> moles/hr	Selectivity moles %
1)	5,1	0	4,0	218	7,3	72,1
2)	5,3	50,3	4,0	243	5,8	66,1
3)	40,0	0	4,0	215	7,0	76,5
4)	40,1	10,0	4,0	218	7,1	75,9
5)	40,1	30,0	4,0	219	7,1	73,6
6)	40,1	50,5	4,0	223	7,2	73,6
7)	40,0	50,2	4,1	246	7,0	69,6

The tests showed the following trends:

at low ethylene concentration (about 5% the presence of CO<sub>2</sub> deeply decreased both the activity and the selectivity of the catalyst; said negative effects decreased remarkably and acceptably for 40% of ethylene.

*The word "downstream" is recognized  
as a Registered Trade Mark.*

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The claims defining the invention are as follows:-

1. A process for the oxidation of ethylene to ethylene oxide with pure oxygen or a mixture containing oxygen at a temperature ranging from 100 to 400°C and at a pressure ranging from 0.7 to 35 atmospheres comprising reacting ethylene at a concentration of from 40 to 80% in the presence of a catalyst constituted by Ag, Ca and Ba, the ratio between the gram atoms of Ag and the sum of gram atoms of calcium and barium being equal to or greater than 1.
2. A process according to claim 1 in which the ethylene/oxygen ratio is higher than 3.
3. A process according to claim 1 in which the ratio between the gram atoms of Ag and the sum of gram atoms of Ca and Ba is in the range of from 4 to 15.
4. A process according to claims 1 and 3 wherein the Ag/Ca/Ba gram atomic ratio is 15/2.5/1.
5. A process according to claims 1, 3, 4 wherein the catalyst is supported on porous alumina having a spherio shape, pores radii ranging from 100 to 700 microns, a volume porosity of about 50%, and the following composition:  

Al <sub>2</sub> O <sub>3</sub>	85.50;	TiO <sub>2</sub>	0.10;	SiO <sub>2</sub>	0.03;
SiO <sub>2</sub>	12.40;	MgO	0.60;	K <sub>2</sub> O	0.50;
Fe <sub>2</sub> O <sub>3</sub>	0.80;	CaO	0.40;	and said porous alumina	

by X-ray analysis shows an alumsino-sillite structure.
6. A process according to any one of claims 1 to 4 wherein said catalyst is supported on a ceramic carrier.
7. A process according to claim 5 or 6 wherein the catalyst supported on a carrier is one which has been prepared by preparing an aqueous solution comprising silver, calcium and barium salts, precipitating silver, calcium and

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barium metals from said aqueous solution, preparing a powder of said precipitated silver, calcium and barium metals, preparing a suspension of said powder, distributing said powder on a carrier and drying the powder on said carrier.

8. A process according to any one of the preceding claims wherein said oxidation is carried out in the presence of ethane.

9. A process according to claim 8 wherein the ethane is present in a concentration of up to 5%.

10. A process according to claim 9 wherein the ethane is present in a concentration up to 30%.

11. A process according to any one of the preceding claims wherein the oxygen is in a concentration from 0% up to explosive limits.

12. A process according to any one of the preceding claims wherein carbon dioxide is present in a concentration of 7% to 60%.

13. A process according to any one of the preceding claims wherein an inhibitor is present.

14. A process according to claim 13 wherein the inhibitor is an organic halogenated compound.

15. A process according to claim 14 wherein the inhibitor is present in an amount less than 0.3 ppm.

16. A process according to claim 15 wherein the inhibitor is present in an amount ranging from 0.01 to 0.3 ppm.

17. A process according to claim 1 as herein described with reference to the Examples.

18. A process according to claim 1 as herein described with reference to the drawing.

19. Ethylene oxide when produced by the process defined

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in any one of the preceding claims.

DATED: 20th August, 1974

GRAN PROGETTI S.P.A.  
By its Patent Attorneys:  
PHILLIPS ORMOND AND FITZPATRICK

*David P. Fitzpatrick*



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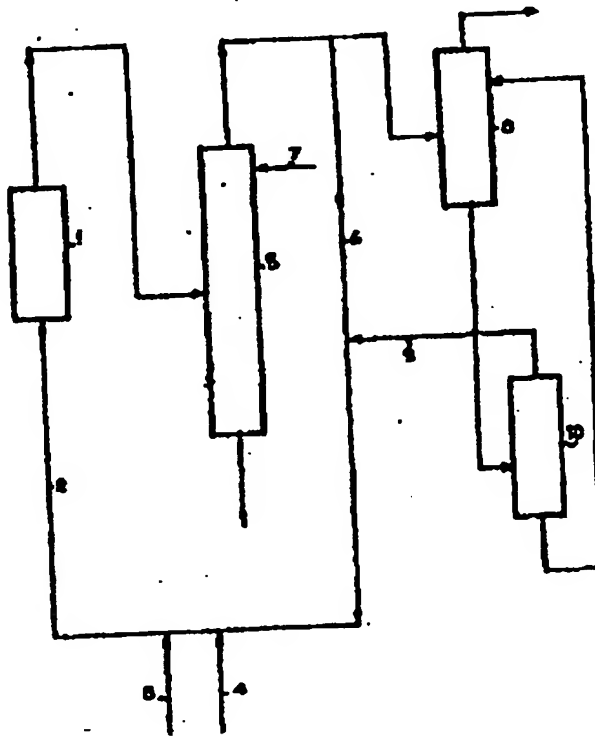


Fig. 1

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